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DETECTION OF MATRIX STRESSES IN GRAPHITE/EPOXY COMPOSITES BY X--ETC(U)
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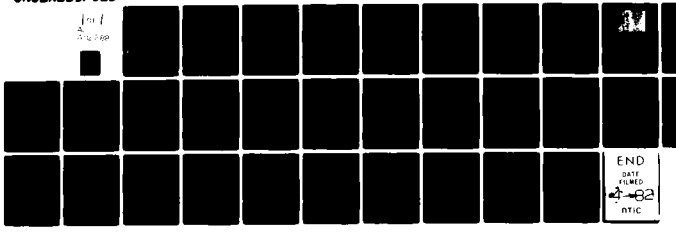

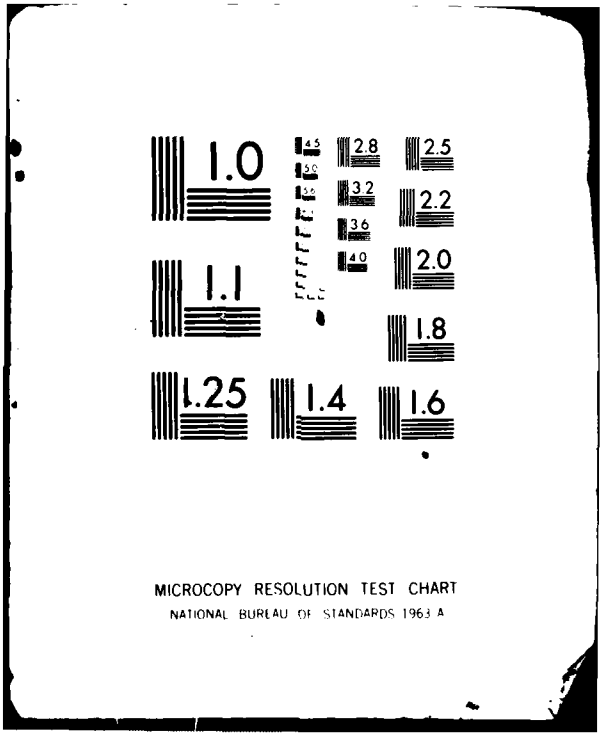
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

X-ray diffraction from graphite fiber/epoxy composite specimens containing fillers measures applied and residual stresses. Similarly, diffraction from filled epoxy painted on specimens measures applied stresses. Both methods indicate moisture content. Both methods measure the stress distribution in the adherends of adhesive bonds, and a modification could also apply to the stresses in the adhesive.

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Grant No. AFOSR 77-3284
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DETECTION OF MATRIX STRESSES IN GRAPHITE/EPOXY COMPOSITES BY X-RAY DIFFRACTION FROM CRYSTALLINE FILLERS
(Unclassifed)

- Submitted to -

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December 1981

ABSTRACT OF TECHNICAL RESULTS

Results obtained during the period 3/1/80-8/31/81 are reported in the two manuscripts of the appendix to this final report and also are covered in the Final Report summary statements below.

An X-ray diffraction method was devised for determining residual and applied stresses in composites by diffraction from embedded filler particles. It has been investigated using a series of different fillers embedded between the first and second plies of 6 ply uniaxial graphite/epoxy laminates. The X-ray diffracted beam shifts were measured when samples were stressed in the fiber direction by a tensile frame mounted on a diffractometer. Within an elastic range up to a filler yield point the stresses in the particles were proportional to the composite stresses in agreement with the model of H. T. Hahn, though smaller than would be expected if the volume fraction of filler were zero. Diffracted beam shifts with applied stress for different fillers increased in the order W, CdO, Ni, Ag, Nb, Al. Theory is in accord with the data. After stressing beyond the yield point and unloading there were residual compressive stresses in the particles in the fiber direction and the yield point in subsequent loadings was raised. The technique developed in this project for determining by X-rays the three principal strains and stresses in the specimens, showed highest stresses (always tensile) in the fiber direction.

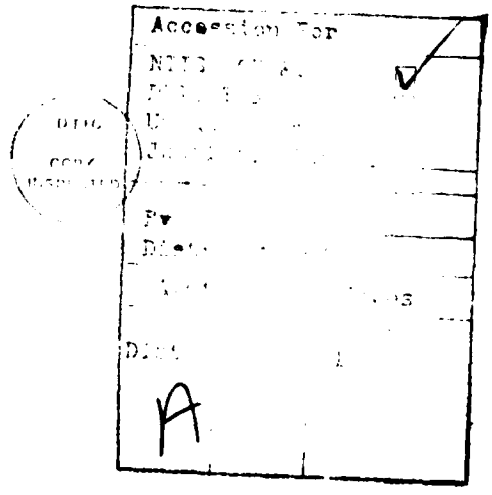
In an epoxy matrix containing a small volume percent of Al filler particles but no fibers, the ratio of matrix stress to stress in the filler (i.e. the Hahn factor, n) was found to be 0.41, in accord with calculations based on Hahn's model. In fiber reinforced composites, n was near 0.2 for Al, Ag and Nb fillers.

In unidirectional graphite-fiber/epoxy laminates with Al particles between the first and second plies the residual stresses in the particles resulting from curing were found to be 5, -34 and -53 MPa in fiber, transverse and thickness directions, respectively, in a specimen dried 7 days at 50°C. Residual stresses in the resin were computed from tensile data and the residual stress data from the particles. Residual stresses in Al particles of a quasi-isotropic $(0, +60, -60)_s$ laminate, which were 46, 47 and -26 MPa in fiber, transverse and thickness directions, respectively, were not reduced by annealing either in the ambient or in a desiccator at temperatures between 50°C and 175°C. When laminate specimens were bent in a three-point bending jig with bends in the range beginning to cause visible and audible damage, it was found upon removal from the jig that pronounced diffraction-angle shifts remained, decreasing with increasing distance from the highest stressed position out to place[illegible]d the loading points.

Diffraction angles were strongly influenced by moisture content, suggesting the method could be developed as a non-destructive test for moisture content. In quasi-isotropic specimens residual stresses parallel to the surface were tensile when the specimens were dry but were reduced to zero by holding about 150 hrs in 100% relative humidity at 50°C. Substantial stresses remain after 490 hrs at 50°C and 55% relative humidity. There was evidence that the stresses depend to some extent on the moisture history of the specimen. Correlations between the X-ray data and moisture diffusion data were made.

Another X-ray method, also nondestructive, was developed that is viable for measuring applied (not residual) stresses, and for detecting delamination. A thin layer of epoxy paint containing a suitable filler is applied to specimens and cured. Diffraction of $CuK\alpha_1$ X-rays from such paint filled with aluminum or silver powders yields shifts in the diffracted peak position, 2θ, shifts that are, in the low stress range, proportional to the magnitude of applied stresses; 2θ undergoes abrupt changes when delamination occurs. Throughout the stress range below the delamination stress, unloading leaves residual 2θ shifts, indicating residual stresses in the filler particles. Three-point bending yielded residual diffraction angle shifts analogous to those obtained with embedded fillers, mentioned earlier. To relate residual angle shifts to stresses resulting from applied loads in calibration tests, the same moisture content and temperature should be used, since both of these parameters can be expected to strongly influence the diffraction angles from fillers in paint, as they do with fillers embedded between plies. (It is suggested that it may be possible to infer something of the stress and moisture-content history of a specimen if data from a specimen subjected to live loads in the field are compared with data from suitable control samples.) This method of stress measurement might find applications to objects that diffract poorly such as glass, rocks, or cement in which a filler has not previously been embedded.

Both of these methods were found to disclose the distribution of stresses over the surface of adhesively bonded joints when light loads were applied and thus could serve to check theoretical stress distributions in the adherends and serve as a non-destructive test for bond defects. Aluminum strips were bonded in a single lap joint and loaded in tension with a load ($\sim$ 8 KSI) well within the elastic limit. Traverses along the bond giving the distribution of the X-ray-measured stresses showed clear evidence of the way in which stress was transferred from one adherend to the other and indicated the limits of the bonded area, together with attendant bending stresses resulting from the loading, which were sharply peaked at the ends of the bond. We suggest that by putting a filler in the adhesive of a joint the stress distribution within the adhesive could be revealed. We are investigating this possibility under a different research grant.



PUBLICATIONS RESULTING FROM THE RESEARCH ON

GRANT NO. AFOSR 77-3284

(Mar. 1, 1977 - Aug. 31, 1981)

1. Charles S. Barrett and Paul Predecki, "Measuring Triaxial Stresses in Embedded Particles by X-Ray Diffraction," Advances in X-Ray Analysis, 21, 305-307 (1978).

2. Paul Predecki and Charles S. Barrett, "Stress Measurement in Graphite/Epoxy Composites by X-Ray Diffraction from Fillers," J. Composite Matls. 13, 61-71 (1979).

3. C. S. Barrett and Paul Predecki, "Stress Analysis in Graphite/Epoxy," (Note). Advances in X-Ray Analysis 23, 331-332 (1980).

4. Paul Predecki and Charles S. Barrett, "X-Ray Stress Measurement in Graphite/Epoxy Composites," Proceedings of the DARPA/AFML Review of Progress in Quantitative NDE. 5th Annual Report AFWAL-TR-80-4078, pp. 225-227, July 1980.

5. Charles S. Barrett and Paul Predecki, "Stress Measurement in Graphite/Epoxy Uniaxial Composites," Polymer Composites, Vol. 1, No. 1,

6. C. S. Barrett and Paul Predecki, "X-Ray Diffraction Evaluation of Adhesive Bonds and Damage in Composites," presented at the ARPA/AF Review of Progress in Quantitative NDE Conference July 13-17, 1980, La Jolla, to be published in Conference Proceedings.

7. Charles S. Barrett and Paul Predecki, "X-Ray Diffraction Evaluation of Adhesive Bonds and Stress Measurement with Diffracting Paint." Advances in X-Ray Analysis 24, 231-238 (1981).

8. Paul Predecki and Charles S. Barrett, "Residual Stresses in Resin Matrix Composites." Presented to and submitted for publication in proceedings of Sagamore Conference, Lake Placid, New York, July 13-17, 1981.

9. Paul Predecki and Charles S. Barrett, "Detection of Moisture in Graphite/Epoxy Laminates by X-Ray Diffraction." Submitted to J. Composite Matls., 1981.

RESIDUAL STRESSES IN RESIN MATRIX COMPOSITES*

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ABSTRACT

By embedding crystalline filler particles in resin matrix laminates during layup, strains that are transferred to the particles were measured by X-ray diffraction. In tensile tests of unidirectional graphite-fiber/epoxy laminates with Al particles between the first and second plies the X-ray strains increased linearly and reversibly with applied stress up to stress levels that initiated yielding in the filler. Residual stresses in the particles resulting from curing were found to be 5, -34 and -53 MPa in fiber, transverse and thickness directions, respectively, in a specimen dried 7 days at 50°C. Residual stresses in the resin were computed from tensile data and the residual stress data from the particles; neglecting transverse stresses, the residual stress in the fiber direction in the resin was computed to be 8.1 MPa (1.2 ksi). Differential thermal contraction from 177°C to 21°C of matrix and fibers in the absence of particles would lead to a prediction of 25 MPa (3.6 ksi); the former computed value for the filled composite was smaller than this presumably in part because of the inhibition of the contraction of the matrix by the closely spaced particles in the layer between the plies. The difference between the residual stresses in the lateral and thickness directions is also ascribed to this particle interaction. Residual stresses in Al particles of a quasi-isotropic $(0, +60, -60)_s$ laminate were not reduced by annealing either in the ambient or in a desiccator at temperatures between 50°C and 175°C; after annealing one hr at 175°C they were 42 and 40 MPa along 0° and 90° directions in the plane of the specimen,

*Work supported by the AFOSR on grant #77-3284.

respectively, and -29 MPa normal to this plane. Diffraction angles were strongly influenced by moisture content, suggesting the method could be developed as a non-destructive test for moisture content. In quasi-isotropic specimens residual stresses parallel to the surface were tensile when the specimens were dry but were reduced to zero by holding about 150 hrs in 100% relative humidity at 50°C. Substantial stresses remain after 490 hrs at 50°C and 50% relative humidity. There was evidence that the stresses depend to some extent on the moisture history of the specimen. Correlations between the X-ray data and moisture diffusion data were made.

INTRODUCTION

Residual stresses in resin matrix composites are of particular interest since, first, they are an unavoidable consequence of curing the resin at elevated temperatures and second, they are affected by environmental exposure, in particular moisture absorption by the resin.

The residual stresses are of two types: (1) micro-stresses in each of the two constituent phases within a given ply. These arise because of differences in thermal and moisture expansion between the two phases. (2) macro-stresses in each ply considered as a homogeneous entity having anisotropic thermal and moisture expansion. These arise because of the constraints of neighboring plies. Macro-stresses have been measured using strain gages embedded in various plies during layup[1] and from warping deflection measurements of asymmetric laminates.[2] They have also been calculated from laminated plate theory.[3]

Data on micro-stresses are less common. Measurements have been made by photoelastic methods using mostly single fiber samples.[4,5] More recently a finite element calculation has been made by Adams and Miller[6] using a square lattice model with a fiber volume of 40%.

The purpose of this study was to develop a practical method for detecting micro-residual stresses in graphite/epoxy laminates using X-ray diffraction. Since neither of these two phases diffract X-rays satisfactorily for strain measurement, the approach taken was to incorporate small amounts of crystalline filler particles into the laminate during layup. The strains transferred to these particles by the resin can then be determined by conventional X-ray diffraction methods.

An advantage of the method is that there is some latitude in the choice of filler particles: fillers can be chosen with sharp diffraction peaks in the back reflection region and with reasonably isotropic elastic properties. Disadvantages are that neither

the strains nor the stresses in the particles are the same as the corresponding quantities in the surrounding resin. It is therefore necessary to calibrate the method using applied stresses. Secondly the presence of the particles perturbs the residual stresses in the vicinity of the particles.

PRINCIPLE OF THE METHOD

The principle of the method is illustrated in Fig. 1. Small amounts (about one monolayer) of particles with suitable diffracting characteristics are placed between any desired pair of plies of a 6 ply graphite/epoxy laminate during layup. During curing some of these particles bleed out with the resin in the plane of the laminas but there is negligible migration in the transverse direction as shown in Fig. 2. If the particles are large compared with the fiber diameter there is a noticeable disruption of the laminate structure; if they are small the disruption is greatly reduced but there is still negligible particle migration in the transverse direction. After a specimen is cured and equilibrated with the desired relative humidity a collimated X-ray beam of known wavelength is diffracted at large angles from the filler particles within the specimen. The interplanar spacing, $d_{\phi,\psi}$ of the planes which are diffracting is then obtained via the Bragg law. A similar determination is made on unstressed particles of the identical filler powder yielding the unstressed interplanar spacing d_u for the same set of planes. The elastic strain, $\varepsilon_{\phi\psi}$ in

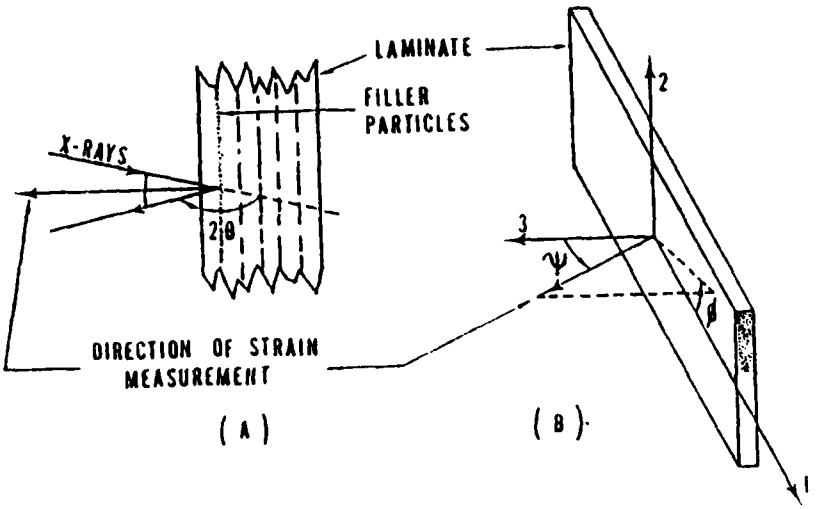

Fig. 1. (A) Representation of diffraction conditions. (B) Direction of strain measurement with respect to laminate axes.

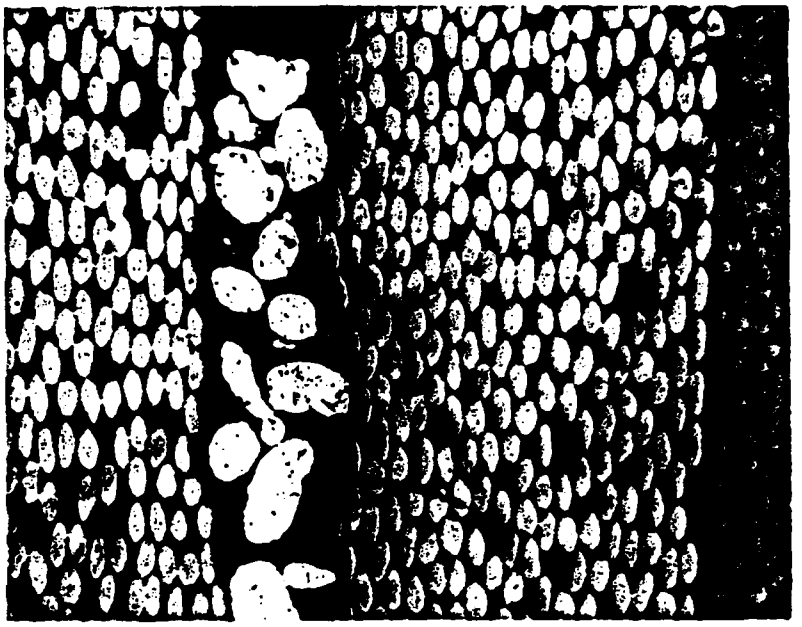

Fig. 2. Cross section of a $(0 \pm 60)_s$ graphite fiber/epoxy laminate containing Al particles. Graphite fibers are 6-8μ diameter.

the filler in the direction defined by angles ϕ and ψ (Fig. 1) relative to the laminate orthotropic axes: 1,2,3, is then obtained from $\varepsilon_{\phi\psi} = (d_{\phi\psi} - d_u)/d_u$. If the principal strain directions in the filler particles are assumed to be parallel to the laminate orthotropic axes, the principal strains in the particles: ε_{1p}, ε_{2p}, ε_{3p} are obtained from $d_{\phi,\psi}$ measurements using the following equations:[7]

$$\varepsilon_{1p} = [(d_{o,\psi} - d_u)/(d_u \, Sin^2\psi)] - \varepsilon_{3p}/Tan^2\psi, \qquad \psi \neq 0 \qquad (1)$$

$$\varepsilon_{2p} = [(d_{90,\psi} - d_u)/(d_u \, Sin^2\psi)] - \varepsilon_{3p}/Tan^2\psi, \qquad \psi \neq 0 \qquad (2)$$

$$\varepsilon_{3p} = (d_{\phi,o} - d_u)/d_u \qquad (3)$$

The principal stresses in the particles: σ_{1p}, σ_{2p}, σ_{3p} are then easily obtained, if desired, from isotropic elasticity expressions with the assumption that the filler particles are elastically

isotropic. The method is calibrated by comparing measured particle strains, ε_{ip}, with the corresponding composite strains ε_i^* obtained with strain gages in applied stress experiments.

Earlier work[8,9] had shown that among the cubic fillers investigated Al, Nb, Ag, CdO had the largest stress sensitivities with $CuK\alpha_1$ radiation, i.e. the largest shift in diffracted peak position with applied stress. These data are summarized in Fig. 3. For the metallic fillers, the knees in the curves appear to be associated with yielding of the filler particles in unidirectional laminates. Repeated loading of such a laminate containing Al particles showed the knee of the curve to increase to a higher stress if the stress in the preceding loading exceeded the knee in the preceding loading (Fig. 4). There are some small changes in slope of the initial stress sensitivity curves if preceding loadings have exceeded the knee. These appear to be associated with relaxation in the resin around the particles. If applied loads do not exceed the knee the initial part of the stress sensitivity plot is reversible and reproducible on repeated loadings. It will be shown later that curing stresses transferred to the particles do not exceed the knee for the Al particles. Because of its high stress sensitivity, Al filler was used for all the residual stress work.

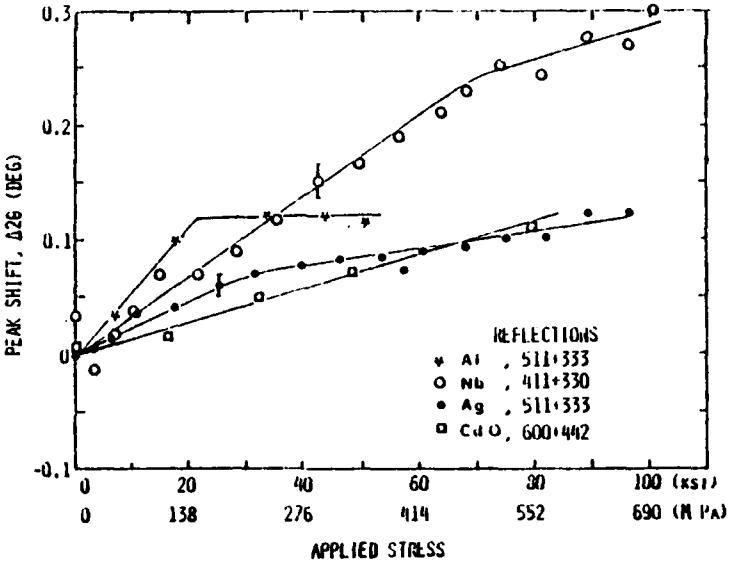

Fig. 3. Shifts in peaks of beams diffracted from various fillers in unidirectional laminates vs. stress applied in fiber direction. $CuK\alpha_1$ radiation, $\phi = \psi = 0$.

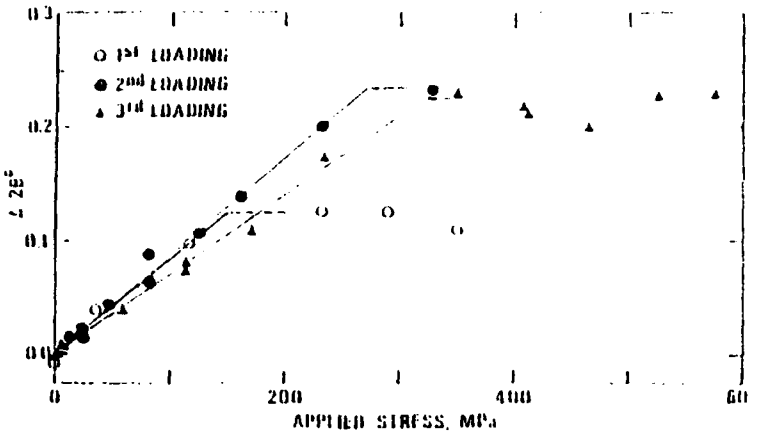

Fig. 4. Diffracted beam peak shift, $\Delta 2\theta$ resulting from repeated loading parallel to the fiber axis. 0° laminate, Al filler, $CuK\alpha_1$ radiation, $\phi = \psi = o$.

EXPERIMENTAL

Two types of 6 ply laminates were laid-up: unidirectional (0°) and quasi-isotropic $(0°,+60°,-60°)_s$. Both had Al particles (-325 mesh) between the first and second plies, and both utilized a graphite/epoxy prepreg: Fiberite T300/934 (Fiberite Corp., Winona, Minn.). Laminates were cured at 350°F (177°C) using the recommended procedures for this prepreg* and then cut into 15.25 x 1.905 x .089 cm tensile samples and 4.45 x 5.08 x .089 cm residual stress samples. Tensile samples had tapered Al (2014-T6) end-tabs attached with epoxy adhesive. A strain gage was then attached near the center of the gage area. Samples were held in clevis type grips in a small tensile frame mounted on a Siemens Krystalloflex II diffractometer as described elsewhere.[8] The diffractometer was modified for diffraction angles 2θ up to 165° and was fitted with a graphite monochromator in front of the counter. The residual stress samples were held in the standard sample holder. Care was taken with both types of sample and with the unstressed Al powder mounted on a glass slide to ensure that the particles irradiated by the X-ray beam were on the axis of the goniometer.

*We are grateful to R. Mirschell, R. Campbell and B. Burke of Martin-Marietta Co., Denver, for fabricating the samples.

Diffracted peak positions were determined using a standard procedure.[10] The upper 1/4 of the 333 plus 511 Al peak obtained with $CuK\alpha_1$ radiation was 5 point step-scanned and a parabola fitted to these points by the least squares method. The apex of the parabola was taken as the peak position. The standard deviation in the determination of peak position by this method was routinely $\pm$ .015°2θ with 2θ around 162.5° using 40 sec counts. For the tensile samples, only two directions of strain measurements were used: $\phi = 0$, $\psi = 0$ and $\phi = 0$, $\psi = 45$. These yielded ε_{1p} and ε_{3p} with the aid of eqs. (1) and (3). For the residual stress samples the direction $\phi = 90$, $\psi = 45$ was added, yielding all three principal strains in the particles.

RESULTS AND DISCUSSION

Curing Stresses

The results of a typical tensile experiment using a unidirectional sample that had been exposed to ambient laboratory conditions for several months are shown in Fig. 5. The X-ray strains

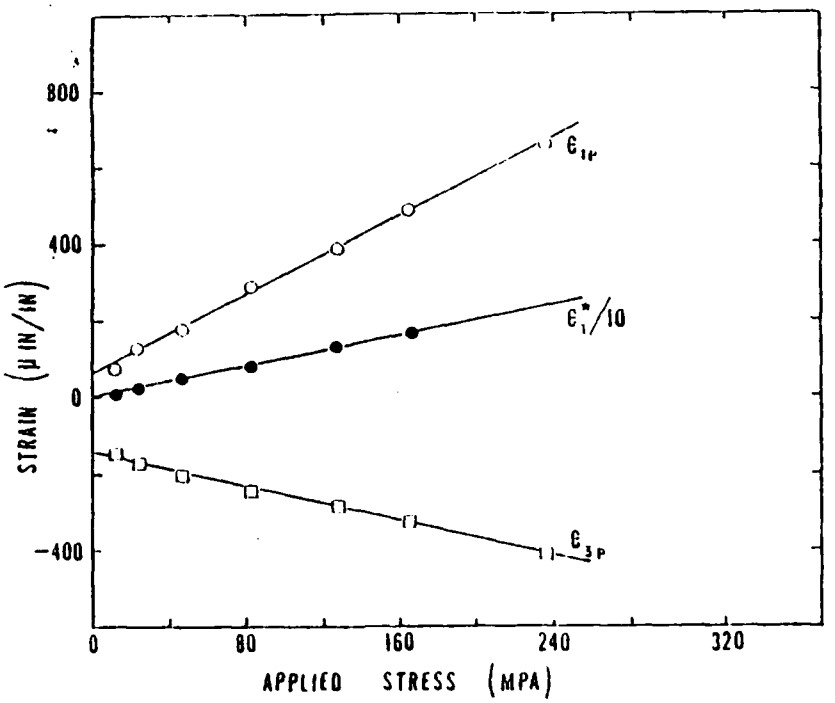

Fig. 5. Linear change in X-ray strains ε_{1p} and ε_{3p} in Al particles embedded in unidirectional composite. Strain gage strain, ε_1^*, is also shown.

in the particles increase linearly with applied stress but do not pass through zero at zero applied stress, indicating the presence of residual stresses. The data in this figure can be used to determine the residual strain ε^r_{1m} in the matrix of other unidirectional samples as follows. As a first approximation we can consider the development of curing stresses to take place in two steps. At the curing temperature (177°C), the system is considered to be stress free. We then consider an element of the matrix containing an Al particle to cool to room temperature in the absence of fibers. During this step the matrix shrinks around the particle since the thermal expansion coefficient of the resin matrix, $\alpha_m = 45 \times 10^{-6}/°C^6$ is greater than that of the particle, $\alpha_p = 23.6 \times 10^{-6}/°C$. The hydrostatic stress, P thereby exerted on the particle at 21°C is given by:[11]

$$P = 3K_p(A-1)B, \qquad (4)$$

assuming elastic isotropic behavior of the particle and the matrix. Here, K_p = bulk modulus of the Al particle taken as 7.66×10^4 MPa, $A = 3K_p/(3K_p + 4\mu_m)$, μ_m = shear modulus of the matrix taken as 1.29×10^3 MPa, $B = (r^o_p - r^o_m)/r^o_m$, r^o_p is the stress free radius of the particle at 21°C and r^o_m is the stress free radius of the hole in the resin at 21°C into which the particle fitted stress free at 177°C. For an Al particle in epoxy resin, eq. (4) gives P = 17 MPa (2.5 ksi). This produces a small mean normal strain $\bar{e} = -75 \times 10^{-6}$ in the particles.

In the second step we consider an applied stress σ^r_{1m} equal to the residual stress which strains the matrix element in the fiber direction by an amount ε^r_{1m} dictated by the stress free fiber length at 21°C. This approach is justified by the fact that the fibers are two orders of magnitude stiffer in the fiber direction than the resin. If σ^r_{1m} is the dominant average stress in the resin and we can neglect transverse stresses, then ε^r_{1m} can be obtained by extrapolating the data of Fig. 5 backward to the point where $\varepsilon_{1p} = \bar{e} = -75 \times 10^{-6}$. This is facilitated by replotting the data of Fig. 5, as shown in Fig. 6. Here the applied composite strain ε^*_{1m} is equal to the incremental matrix strain since the matrix must deform the same amount as the composite in the fiber direction. The principal residual <u>particle</u> strains and stresses obtained on a unidirectional dry laminate (held 7 days in a desiccator at 50°C) were $\varepsilon^r_{1p} = 507 \times 10^{-6}$, $\varepsilon^r_{2p} = -255 \times 10^{-6}$, $\varepsilon^r_{3p} = -610 \times 10^{-6}$ and $\sigma^r_{1p} = 5$ MPa, $\sigma^r_{2p} = -34$ MPa, $\sigma^r_{3p} = -53$ MPa. The strain $\varepsilon^r_{1p} = 507 \times 10^{-6}$ corresponds to a <u>matrix</u> residual strain

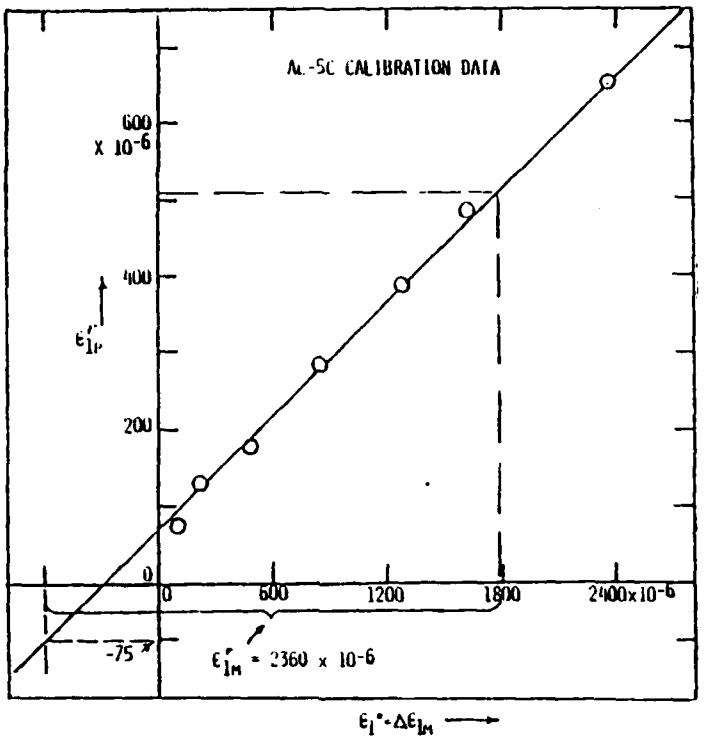

Fig. 6. X-ray strain, ϵ_{lp}, vs composite strain, ϵ_l^*, (= incremental matrix strain, $\Delta\epsilon_{lm}$) from data of Fig. 5.

ϵ_{lm}^r = 2360 x 10^{-6} from Fig. 6. This can be compared with a calculated value of ϵ_{lm}^r using the two step approach but without particles. Thus $\epsilon_{lm}^r = \alpha_m\Delta T - \alpha_f\Delta T$ = 7280 x 10^{-6} and σ_{lm}^r = 25 MPa (3.6 ksi) where α_f is the fiber expansion coefficients in the fiber direction, taken as -1.8 x $10^{-6}/°C$[6] and ΔT = 156°C. The agreement is poor. Furthermore if the measured ϵ_{lm}^r is converted to a stress using a resin modulus of 3.45 x 10^3 MPa, the result is σ_{lm}^r = 8.1 MPa (1.2 ksi) which is substantially less than the value of 26 MPa (3.8 ksi) obtained by Adams and Miller from a finite model.[6] It may be noted in passing that the calculated σ_{lm}^r value from the simple model (3.6 ksi) agrees well with the σ_{lm}^r value of 3.8 ksi obtained by Adams and Miller.[6]

The discrepancy between measured and calculated values is due in part to the fact that there are many particles present in the 1,2 plane. Contraction of the resin in the 2 direction and

development of the full residual tensile stress in the 1 direction are therefore inhibited. An indication of this is shown by the fact that ε^r_{2p} and ε^r_{3p} are not equal, whereas they should be if the matrix behavior was unaffected by the particles. Unidirectional laminates containing no fillers are transversely isotropic.

Similar conclusions were reached with the quasi-isotropic samples where matrix residual strains from X-ray measurements were $\varepsilon^r_{1m} = \varepsilon^r_{2m} = 2800 \times 10^{-6}$ compared with calculated values of 7280 x 10^{-6}.

An obvious improvement in the X-ray method would be to use substantially fewer particles in the 1,2 planes. With present equipment this would necessitate excessively long counting times to be practical. The method was therefore used qualitatively for detecting residual stress changes with environmental exposure.

Attempts to reduce the curing stresses by annealing a quasi-isotropic dry laminate sample at progressively higher temperatures were not successful. After 12 days in a desiccator at 50°C one specimen had $\sigma^r_{1p} = 46$ MPa, $\sigma^r_{2p} = 47$ MPa, $\sigma^r_{3p} = -26$ MPa; after annealing 1 hr each at successively higher temperatures in the ambient another quasi-isotropic specimen had corresponding stresses, respectively, of 42, 40 and -29 MPa after a final anneal at 177°C, and none of the annealing temperatures resulted in a marked reduction of stress as judged by $2\theta_{90,0}$ or occasional full X-ray stress determination.

Effects of Environmental Moisture

It was found that the diffracted peak positions from laminates exposed to dry or moist air were sensitive to the relative humidity and time of exposure. An as-cured quasi-isotropic sample (held two weeks after curing in a sealed polyethylene bag) having Al particles 0.16 mm beneath the sample surface was initially placed in a desiccator (Drierite) at 50°C. It was periodically removed, X-rayed and replaced in the desiccator. After 170 hrs the sample was placed in 100% humid air at 50°C and subsequently removed for brief periods for X-raying. The changes in the diffracted peak position at $\phi = 90$ and $\psi = 0$ with time are shown in Fig. 7. There is a substantial change on going from the fully dry to the fully wet condition which is accompanied by a weight gain of the laminate due to moisture absorption. Samples exposed to more than one drying and wetting cycle have shown that the changes in diffracted peak positions are reversible and roughly superposable, provided the samples reach equilibrium in each condition.

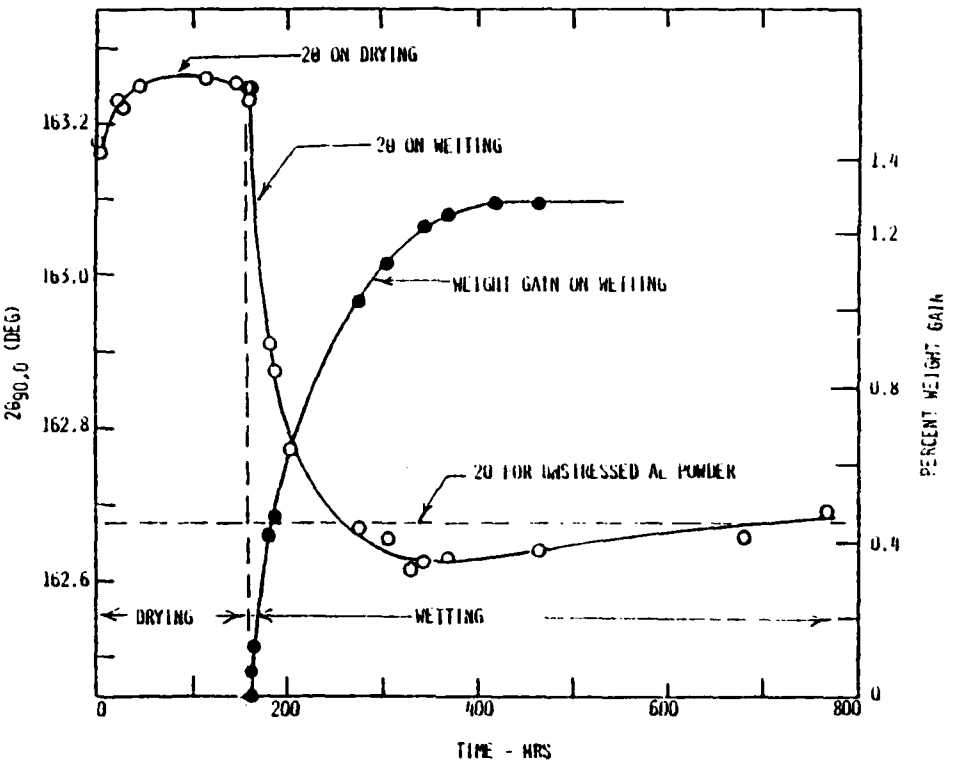

Fig. 7. Changes in weight and diffracted beam position (with ψ = o) from Al particles in $(0°, +60°, -60°)_s$ composite during drying and wetting at 50°C.

In Fig. 8 are shown the changes in the particle residual stresses during the wetting cycle in Fig. 7. It is evident that the in-plane residual stresses σ^r_{1p} and σ^r_{2p} which are initially tensile, decrease to zero in about 150 hrs as a result of moisture absorption by the resin. The remaining stress σ^r_{3p}, initially compressive, rapidly becomes slightly tensile due to swelling of the resin in the 3 direction. Thereafter σ^r_{3p} decays slowly to zero, possibly due to viscoelastic relaxation in the 3 direction. Calculations by Tsai and Hahn[3] based on single lamina hygrothermal properties predict that at room temperature the relative humidity for typical graphite/epoxy composites to be stress free is around 55%. Measurements to date of samples held for extended periods in a humidity controlled chamber (Blue M) show substantial residual stresses are still present after 490 hrs at 50°C and 55% relative humidity. The actual values appear to depend on the moisture history of the samples by somewhat more than statistical error.

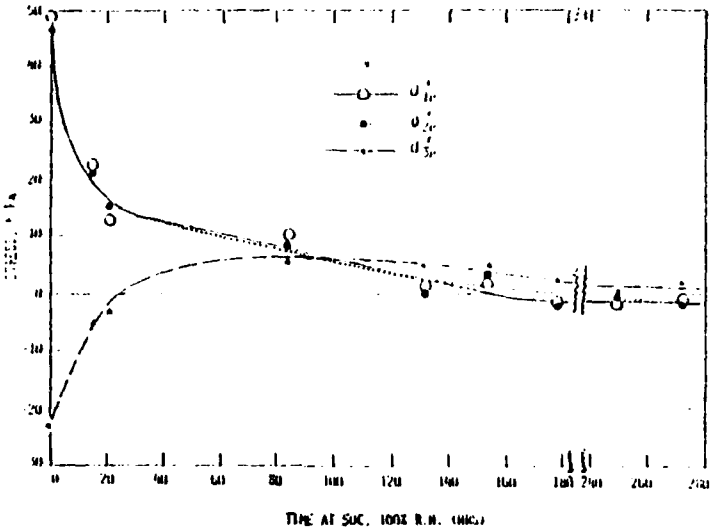

Fig. 8. Residual stress vs time during the wetting cycle of Fig. 7.

The laminate material considered by Tsai and Hahn had a greater moisture absorption capability than found in this study (1.8% equilibrium weight gain at 100% RH versus 1.3%) which may account for the difference.

The correlation between the X-ray measurements and the moisture weight gain indicated in Fig. 7 was examined by plotting the residual particle strain, ε^r_{3p} and the average in-plane particle residual stress, $1/2\ (\sigma^r_{1p} + \sigma^r_{2p})$ against the fractional weight gain, $\bar{C}/C_f$, where C_f is the final or plateau concentration and $\bar{C}$ the average moisture concentration in the laminate. The results are shown in Fig. 9. ε^r_{3p} increases approximately linearly with moisture gain initially, whereas the mean in-plane residual stress decays progressively to zero.

One might expect that the local moisture concentration, $C(x_p,t)$ at the depth x_p below the surface, where the particles are found, would correlate better with the X-ray measurements. To obtain $C(x_p,t)$ we assume that moisture diffusion in the laminates is Fickian as has been shown by Shen and Springer.[12] We obtain first the transverse diffusion coefficient, D_T at 50°C from the weight gain data of Fig. 7. This was done by plotting the weight gain data versus $(\text{time})^{1/2}$ as shown in Fig. 10. From the semi-infinite plate solution,[13] the initial slope of this plot is given by $(4\ D_T{}^{1/2})/(h\pi^{1/2})$ where h is the laminate thickness. Fig. 10 gives $D_T = 15.3 \times 10^{-8}$ mm^2/s, in reasonable agreement with a value

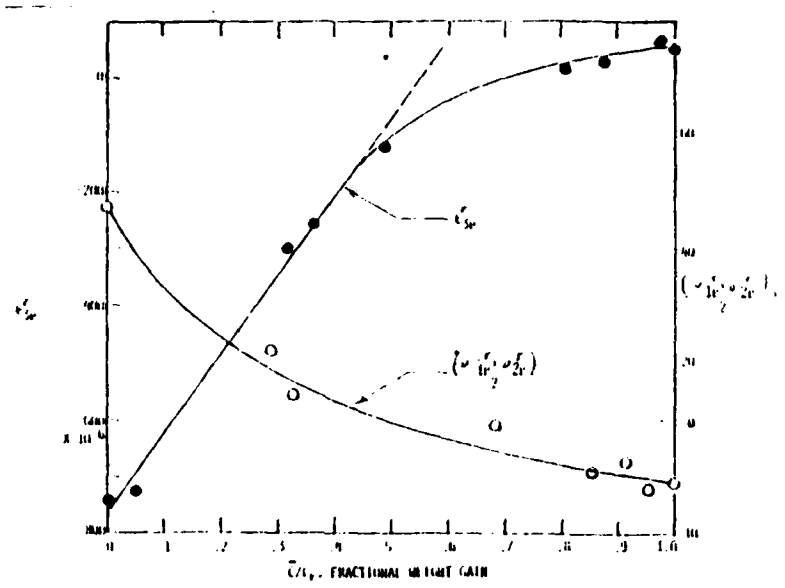

Fig. 9. Average in-plane particle stress, $1/2(\sigma^r_{1p} + \sigma^r_{2p})$ and particle strains, ε^r_{3p} vs fractional weight gain $\bar{C}/C_f$ in $(0°, +60°, -60°)_s$ composite during drying cycle of Fig. 7.

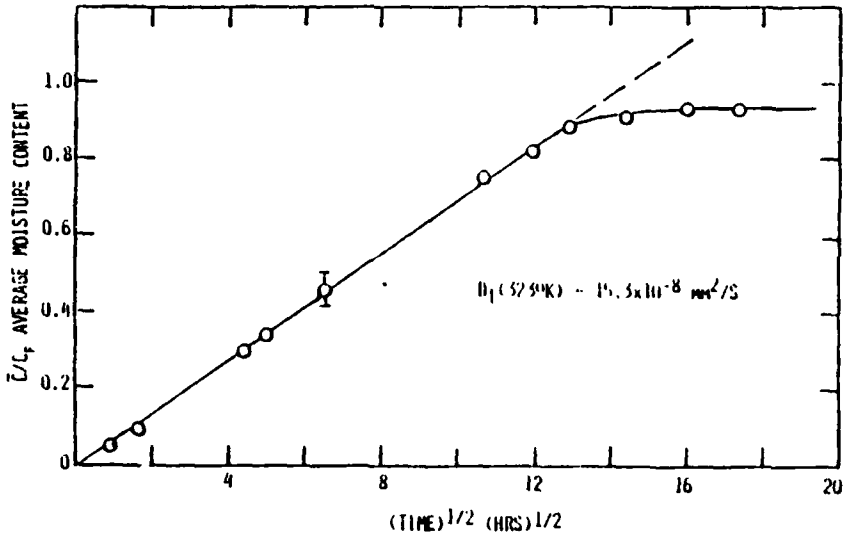

Fig. 10. Linear dependence of average moisture content on square root of time. Data of Fig. 7.

of 11 x 10^{-8} mm^2/s obtained from the resin data of Shen and Springer[12] for a volume fraction fibers of 0.63 measured on our laminates using quantitative metallography.

The local moisture concentration for short times (< 5 hrs in this case) is then given by[13]

$$C(x,t)/C_f = [1 - \text{erf } x/(4D_T t)^{1/2}] \tag{5}$$

For longer times, the expression:[13]

$$C(x,t)/C_f = \left\{1 - \frac{4}{\pi} \sum_{\nu=0}^{\infty} \left(\frac{1}{2\nu + 1}\right) \sin \frac{(2\nu + 1)\pi x}{h} \cdot \exp\left[-\left(\frac{(2\nu + 1)\pi}{h}\right)^2 D_T t\right]\right\} \tag{6}$$

gives C(x,t) with sufficient accuracy when only the first two or three terms in the summation are used. In this expression ν is the summation index.

Using D_T = 15.3 x 10^{-8} mm^2/s, a mean particle depth x_p = 0.16 mm and eqns. (5) and (6), $C(x_p,t)/C_f$ values were obtained and plotted versus ε^r_{3p} and $1/2(\sigma^r_{1p} + \sigma^r_{2p})$ as shown in Fig. 11. The correlation is similar and not any better than that using average moisture concentrations.

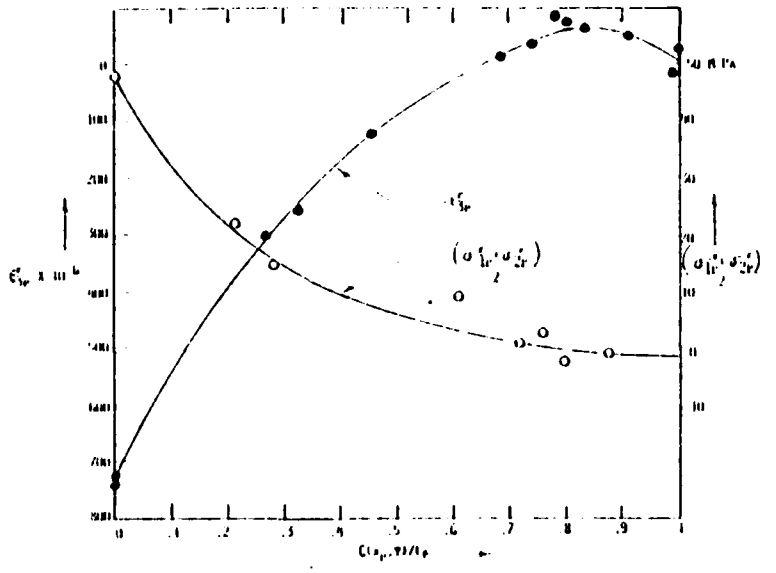

Fig. 11. Moisture concentration at depth of particles, $C(x_p,t)$, relative to final concentration, C_f, vs residual strains ε^r_{3p} and residual stress function $1/2(\sigma^r_{1p} + \sigma^r_{2p})$.

CONCLUSIONS

The X-ray diffraction method described provides a relatively sensitive indication of micro-residual stresses in the resin phase of resin matrix composites. The method is sensitive to moisture absorbed by the resin from the environment and could be developed as a non-destructive method for that purpose. In-plane curing stresses detected by the method show no indication of being reduced by annealing.

In its present form the method does not give the true residual stresses in the resin. This appears to be because the number of particles present in the plane between the first and second plies was large enough to perturb the resin behavior in the vicinity of the particles. This deficiency can probably be overcome by using substantially fewer diffracting particles but would necessitate a more rapid X-ray stress measuring system than the conventional diffractometer system used in this study.

REFERENCES

1. I. M. Daniel, "Residual Stresses in Angle-Ply Polymer Matrix Composites," Proceedings of Nondestructive Evaluation of Residual Stress Workshop, San Antonio, Aug. 1975, pp. 111-121. Report NTIAC-76-2.
2. H. T. Hahn and R. Y. Kim, "Swelling of Composite Laminates." Technical Report AFML-TR-77-199. December 1977.
3. S. W. Tsai and H. T. Hahn, "Introduction to Composite Materials." Technomic Publishing Co., 1980, Ch. 8.
4. L. J. Broutman and F. J. McGarry, Modern Plastics 40(1):161 (1962).
5. B. W. Rosen in "Fiber Composite Materials." ASM, Metals Park, Ohio, Ch. 3, p. 59 (1964).
6. D. F. Adams and A. K. Miller, "Hygrothermal Microstresses in a Unidirectional Composite Exhibiting Inelastic Material Behavior." J. Composite Matls 11:285-99 (1977). Also A. K. Miller and D. F. Adams, Mechanical Engineering Dept., Univ. of Wyoming report #UWME-DR-7011111, Jan. 1977 for numerical values.
7. C. S. Barrett and Paul Predecki, "Measuring Triaxial Stresses in Embedded Particles by Diffraction." Advances in X-Ray Analysis, Plenum Publ. Corp., New York 21:305 (1978).
8. Paul Predecki and Charles S. Barrett, "Stress Measurement in Graphite/Epoxy Composites by X-ray Diffraction from Fillers." J. Composite Matls. 13:61-71 (1979).
9. Paul Predecki and Charles S. Barrett, "X-Ray Stress Measurement in Graphite/Epoxy Composites," to be published in the Proceedings of the ARPA/AF Review of Progress in Quantitative NDE. July 8-13, 1979.

10. Soc. of Automotive Engineers Information Report SAE J 784a (1971).
11. J. W. Christian, "The Theory of Transformations in Metals and Alloys," Pergamon Press, p. 190-192 (1965).
12. C-H. Shen and G. S. Springer, "Moisture Absorption and Desorption of Composite Materials." J. Composite Matls. 10:2-20 (1976).
13. W. Jost, "Diffusion in Solids, Liquids, Gases." Academic Press, Chapter 1 (1960).

DETECTION OF MOISTURE IN GRAPHITE/EPOXY LAMINATES BY X-RAY DIFFRACTION*

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ABSTRACT

The objective of this study was to determine if X-ray diffraction could be utilized to detect moisture non-destructively in graphite/epoxy laminates. $CuK\alpha_1$ X-rays were diffracted from 333 + 511 planes of Al particles embedded between the first and second plies of $[0 \pm 60]_s$ laminates during layup. Diffracted peak positions were quite sensitive to environmental moisture; decreasing 0.624° ± .015°2θ on going from a completely dry to a completely wet state at 50°C. The changes were reversible. Correlations between in-plane, residual particle strains and both average and local moisture content of the laminate were obtained. Annealing effects were investigated.

INTRODUCTION

The moisture content of resin matrix laminates is normally calculated from theory using Fickian diffusion equations, if the temperature and relative humidity history of the laminate is known. Evidence for the validity of this approach has been obtained from moisture weight gain/loss experiments [1]. Moisture content has also been determined by direct

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chemical methods but these usually require removal of a sample from the laminate. In this paper we describe briefly an X-ray diffraction method for detecting moisture via the changes in residual strains in crystalline filler particles which are embedded in the matrix during layup.

In earlier work [2] we have shown that particles embedded between the first and second plies of unidirectional laminates act as useful indicators of residual and applied stress in the laminates. The principal elastic strains in the particles are measured by X-ray diffraction and are related to laminate stresses by calibration experiments using known applied loads.

In this work, the observed sensitivity of the residual elastic strains in such filler particles to the moisture history of the laminate was investigated further.

EXPERIMENTAL

Six ply, quasi-isotropic $(0°, \pm 60°)_s$ laminates were laid up using Fiberite T300/934 (Fiberite Corp., Winona, Minn.) graphite epoxy prepreg. Aluminum particles of -325 mesh were introduced between the first and second plies during layup by spreading a thin layer of these particles on the first green ply and shaking off particles which did not adhere. Laminates were cured at 177°C (350°F) using procedures recommended for this prepreg.* Residual stress samples 4.45 x 5.08 x .089 cm thick were then cut from the laminates and stored in sealed polyethylene bags prior to use.

Samples were exposed to various humidities in a controlled humidity chamber at 50°C (Blue M model VP, 100RAT-1 Blue Island, Ill.). Zero

*We are grateful to R. Mirschell, R. Campbell and B. Burke of Martin-Marietta Co., Denver, for fabricating the samples to our specifications.

humidity samples were placed in a container with $CaSO_4$ (Drierite) at 50°C. Samples were periodically removed and X-rayed or weighed in ambient laboratory conditions and replaced in the controlled humidity chamber.

The residual strains in the filler particles were measured using procedures described elsewhere [2,3]. Samples were held in the standard sample holder of a Siemens Krystalloflex 4 diffractometer. The counter holder was modified for diffraction angles, 2θ, up to 165° and fitted with a monochromator. Aluminum powder identical to that used in the laminates was used as a stress free standard and was positioned in the sample holder in exactly the same plane as the filler particles of the sample (which were 0.16 mm below the sample surface). Diffraction peak positions of the 333 plus 511 Al peak (around 162.7°2θ) were determined by fitting a parabola to five step-scanned points on the top 1/4 of the peak from each sample [4] at room temperature. All 2θ's were corrected to 22.2°C, using a correction of 0.010°2θ per degree F, obtained from the thermal expansion coefficient of aluminum. Each peak determination required 10 to 15 mins. Peaks were measured in three directions relative to the sample geometry yielding the residual particle strains, $\varepsilon_{\phi\psi}$, at $\phi = 0 = \psi$, $\phi = 0$ $\psi = 45$ and $\phi = 90$ $\psi = 45$. The angles ϕ and ψ are defined in Fig. 1. From these the principal residual strains, ε^r_{ip}, (i = 1-3) in the particles were calculated assuming the laminate orthotropic axes, 1, 2, 3, were the principal axes. The in-plane strains ε^r_{1p} and ε^r_{2p} were almost identical as expected for the quasi-isotropic laminate. The standard deviation in determining peak positions was ± .015°2θ which corresponds to a standard deviation in the measured strains of $\pm 56 \times 10^{-6}$.

RESULTS AND DISCUSSION

The changes in the diffracted peak position, $2\theta_{90,0}$, measured at $\phi = 90$, $\psi = 0$ with time are shown in Fig. 2. Initially at time = 0, the peak position is quite high, ∿ 163.17 relative to the unstressed Al powder,

indicating a dry sample, as might be expected for the as-cured laminate stored 2 weeks in a sealed polyethylene bag. Further drying in Drierite at 50°C further increased the peak position slightly. After 170 hrs in 0% humidity this sample was placed in 100% humid air at 50°C. There was an immediate and pronounced decrease in peak position accompanied by a weight gain of the laminate due to moisture absorption. The weight gain reached a plateau at $\sim$ 1.3% about 230 hrs after the start of the wetting cycle, whereas the $2\theta_{90,0}$ value went through a minimum and then equilibrated after $\sim$ 500 hrs at approximately the value for the unstressed Al powder. Samples exposed to more than one such 0% RH drying/100% RH wetting cycle have shown that the changes in $2\theta_{90,0}$ are reversible and approximately superposable, provided the samples reach equilibrium in each condition.

The $2\theta_{90,0}$ data for a wetting cycle such as shown in Fig. 2, together with $2\theta_{0,0}$ and $2\theta_{90,0}$ data simultaneously taken, were converted to particle strains and the results plotted in Fig. 3. It is evident that the in-plane residual strains ε^r_{1p} and ε^r_{2p} which are initially tensile, decrease to zero in 100 to 150 hrs as a result of moisture absorption by the resin. At short times one might expect ε^r_{2p} to decrease more rapidly than ε^r_{1p} since the 0° plies are outermost and the laminate should experience initially a larger strain in the 2 direction than in the 1 direction [5]. This effect was not detected in the X-ray measurements.

The third strain, ε^r_{3p}, initially compressive, becomes slightly tensile presumably due to swelling of the resin in the 3 direction, before decaying to zero at longer times. This decay is thought to be the result of visco-elastic relaxation of the resin in the 3 direction. Using the nomenclature of Yeow et al. [6], the in-plane particle strains would be expected to be

fiber dominated and therefore time insensitive--apart from the time dependence of moisture uptake. The thickness strain, ε_{3p}^{r}, is resin dominated and would be expected to show relaxation. This relaxation is also evident in Fig. 2 where $2\theta_{90,0}$ peak position continues to decay toward the unstrained state after the weight gain has become constant.

To facilitate use of the method as a probe for laminate moisture content, samples were held at various relative humidities until no further change in diffracted peak position was observed--usually 400-500 hrs. at 50°C. The resulting plot of equilibrium peak position versus relative humidity (Fig. 4) is only linear to a first approximation. The observed scatter was attributable both to sample-to-sample variation and to sample moisture history variation, a scatter that is somewhat more than the statistical error in the measurements. From Fig. 4 it is clear, however, that the relative humidity for producing a stress-free state in the Al filler particles at room temperatures is near 100%. This is also the % R.H. for the laminate to be free of residual stresses since the strains in the particles have been shown to be proportional to applied laminate stresses [2]. (Here we are neglecting the contribution to the particle strain due to thermal and moisture expansion mismatch between the Al and the resin). Calculations by Tsai and Hahn [7] based on single lamina hygrothermal properties for a typical graphite/epoxy laminate, predict the R.H. value for zero residual stress to be around 55%. The laminate material considered by Tsai and Hahn had a greater saturation moisture content than found in this study (1.8% equilibrium weight gain at 100% RH versus our 1.3%) which may account for the difference.

The effect of annealing the laminates below the curing temperature (177°C) was explored to see if any residual strain relief is obtained.

Since an increase in moisture content reduces the diffraction angle $2\theta_{90,0}$ and therefore the residual strains as shown in Figs. 2 and 3, attempts were made to avoid any increase in moisture content during annealing. Two specimens that had been dried in a Drierite desiccator at 50°C (sample 3A for 10 days, sample 3F for 31 days) were annealed for periods of one to two hours at successively higher temperatures; sample 3A in an air oven and sample 3F in a P_2O_5 desiccator. The change in $2\theta_{90,0}$ measured at room temperature as a result of annealing is shown in Fig. 5. From Fig. 5 one may conclude that the samples started with different moisture contents and that the P_2O_5 was more effective in eliminating moisture during anneals than air annealing until temperatures reached 150°C. There was no evidence of a decrease in diffraction angle and therefore in residual strains as a result of annealing.

Returning to Fig. 2, the relation between the X-ray measurements and the moisture weight gain was examined further by plotting the average in-plane particle residual strain; $(\varepsilon_{1p}^r + \varepsilon_{2p}^r)/2$ against the fractional weight gain, $\bar{c}/c_f$, where c_f is the final or plateau moisture concentration in the laminate and $\bar{c}$ is the average concentration at any time during the wetting cycle. The resulting plot shown in Fig. 6 (curve A) is not linear. One might expect that the residual strains would correlate better with the local moisture concentration, $c(x,t)$, at the particular depth $x = x_p = 0.16$ mm below the surface where the particles are located. $c(x_p,t)/c_f$ was obtained assuming Fickian diffusion of moisture in the laminate and using a value of 15.3×10^{-8} mm^2/s for the transverse diffusion coefficient calculated from the weight gain data of Fig. 2 [3]. The resulting correlation shown as curve B in Fig. 6 is similar to and not any better than curve A. The non-linearity may be a consequence of the higher resin content of the layer in which the particles lie. The

non linearity may also be attributed to the changing gradients in moisture concentration and the accompanying stress gradients. These gradients were avoided in the experiments reported in Fig. 4, where approximate linearity was found between % R.H. and changes in 2θ.

CONCLUSIONS

(1) The changes in the diffracted peak positions using $CuK\alpha_1$ radiation and the 333 + 511 planes in Al particles in the laminates are quite sensitive to environmental moisture taken up by the laminates. The reversible change of $0.624°2\theta$ on going from the completely dry to the completely wet condition at equilibrium, compared with an average measurement error of $\pm$ $.015°2\theta$, is sufficiently large to be useful for moisture measurement. The diffracted intensity is sufficient for these measurements to be made at depths up to $\sim$ 0.38 mm beneath the surface with conventional equipment.

(2) The relative humidity which gives zero residual stress at room temperature in the laminates investigated (Fiberite T300/934) is near 100%.

(3) The correlation between the average in-plane residual strain in the particles and the calculated moisture concentration at the depth below the laminate surface where the particles lie is non-linear.

(4) Annealing in either ambient or desiccated air at temperatures below the curing temperature (177°C) serves mainly to remove additional moisture from the laminates and thereby increases the residual strains.

Figure Captions

Fig. 1. (A) Representation of diffraction conditions

(B) Direction of strain measurement relative to laminate axes

Fig. 2. Sensitivity of diffracted beam position (for $\phi = 90$, $\psi = 0$) to environmental moisture at 50°C. Relative humidity was zero during "drying" and 100% during "wetting." The percent weight gain of the laminate during wetting is also shown.

Fig. 3. Changes in principal residual particle strains during the wetting cycle of Fig. 2. Error bars in this and subsequent figures are ± one average standard deviation.

Fig. 4. Roughly linear relation between diffracted peak position (for $\phi = 90$, $\psi = 0$) and relative humidity after equilibrium has been reached. Some sample to sample variation is evident.

Fig. 5. Increase in diffracted peak position (for $\phi = 90$, $\psi = 0$) measured at room temperature, as a result of annealing laminates at successively higher temperatures; sample 3A always in air, sample 3F always in a P_2O_5 desiccator.

Fig. 6. Decrease in average in-plane residual strain in the Al particles with increasing average moisture content of the laminate, $\bar{c}/c_f$, (curve A), and with increasing moisture concentration at the location of the particles, $c(x_p,t)/c_f$, (curve B).

REFERENCES

1. C.-H. Shen and G. S. Springer, "Moisture Absorption and Desorption of Composite Materials," J. Composite Matls., Vol. 10, (1976), p. 2.

2. Paul Predecki and C. S. Barrett, "Stress Measurement in Graphite/Epoxy Composites by X-ray Diffraction from Fillers," J. Composite Matls., Vol. 13, (1979), p. 61.

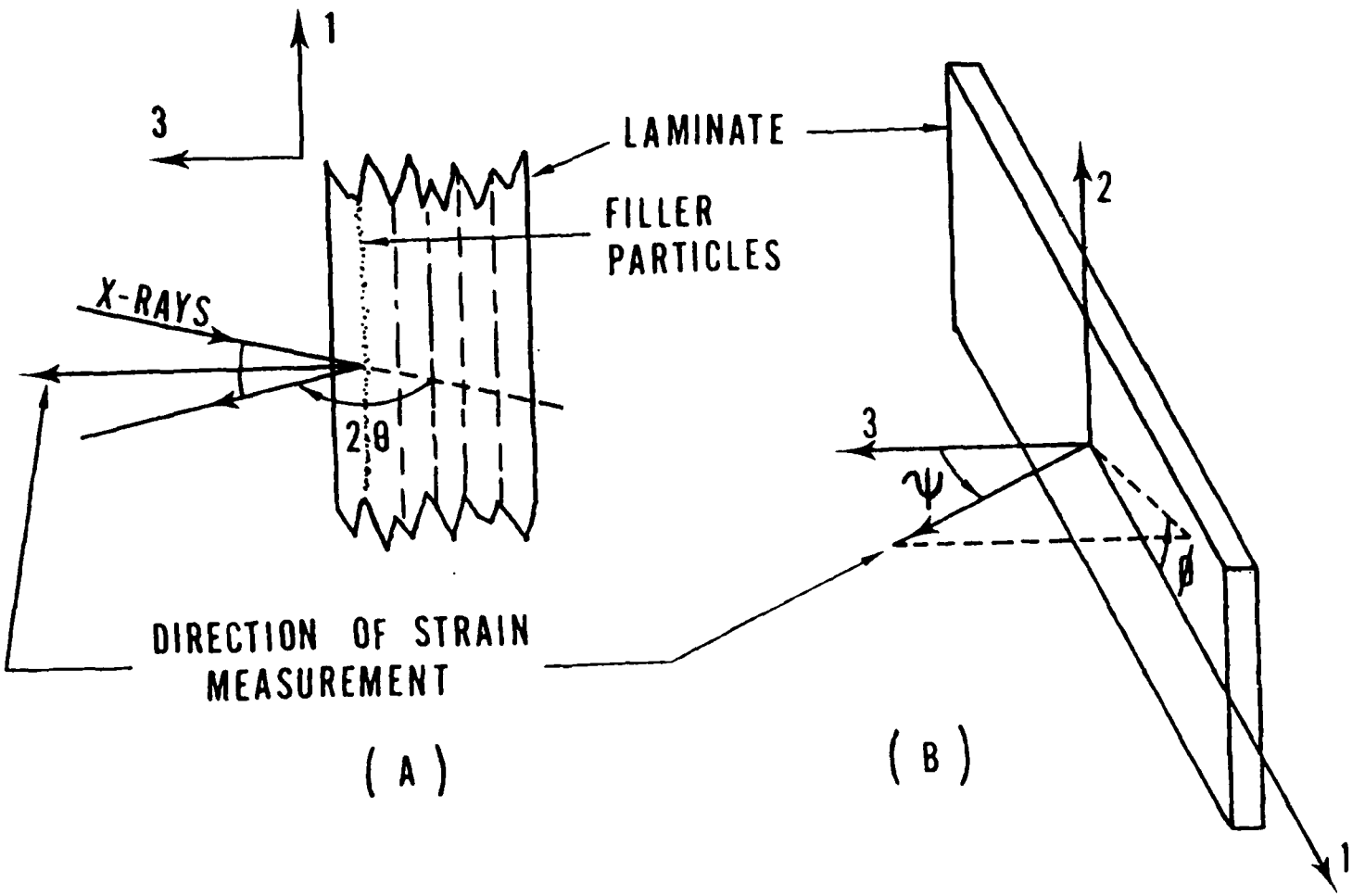
3. Paul Predecki and C. S. Barrett, "Residual Stresses in Resin Matrix Composites." Presented at the 28th Sagamore Army Materials Research Conference, Lake Placid, New York, July 13-17, 1981. To be published in conference proceedings.

4. Soc. Automotive Engineers Information Report SAE J 784a.

5. D. L. Flaggs and F. W. Crossman, "Analysis of Viscoelastic Response of Composite Laminates Durin Hygrothermal Exposure," J. Composite Matls., Vol. 15, (1981), p. 21.

6. Y. T. Yeow, D. H. Morris and H. F. Brinson, "Time-Temperature Behavior of a Unidirectional Graphite/Epoxy Composite" in "Composite Materials: Testing and Design (5th Conference)", S. W. Tsai, Editor. ASTM STP 674, 1979, pp. 263-281.

7. S. W. Tsai and H. T. Hahn, "Introduction to Composite Materials." Technomic Publ. Co., Westport, Conn. (1980), p. 352.


1
3
LAMINATE
FILLER
PARTICLES
X-RAYS
2θ
DIRECTION OF STRAIN
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(A)
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ψ
β
1
(B)

Fig. 1

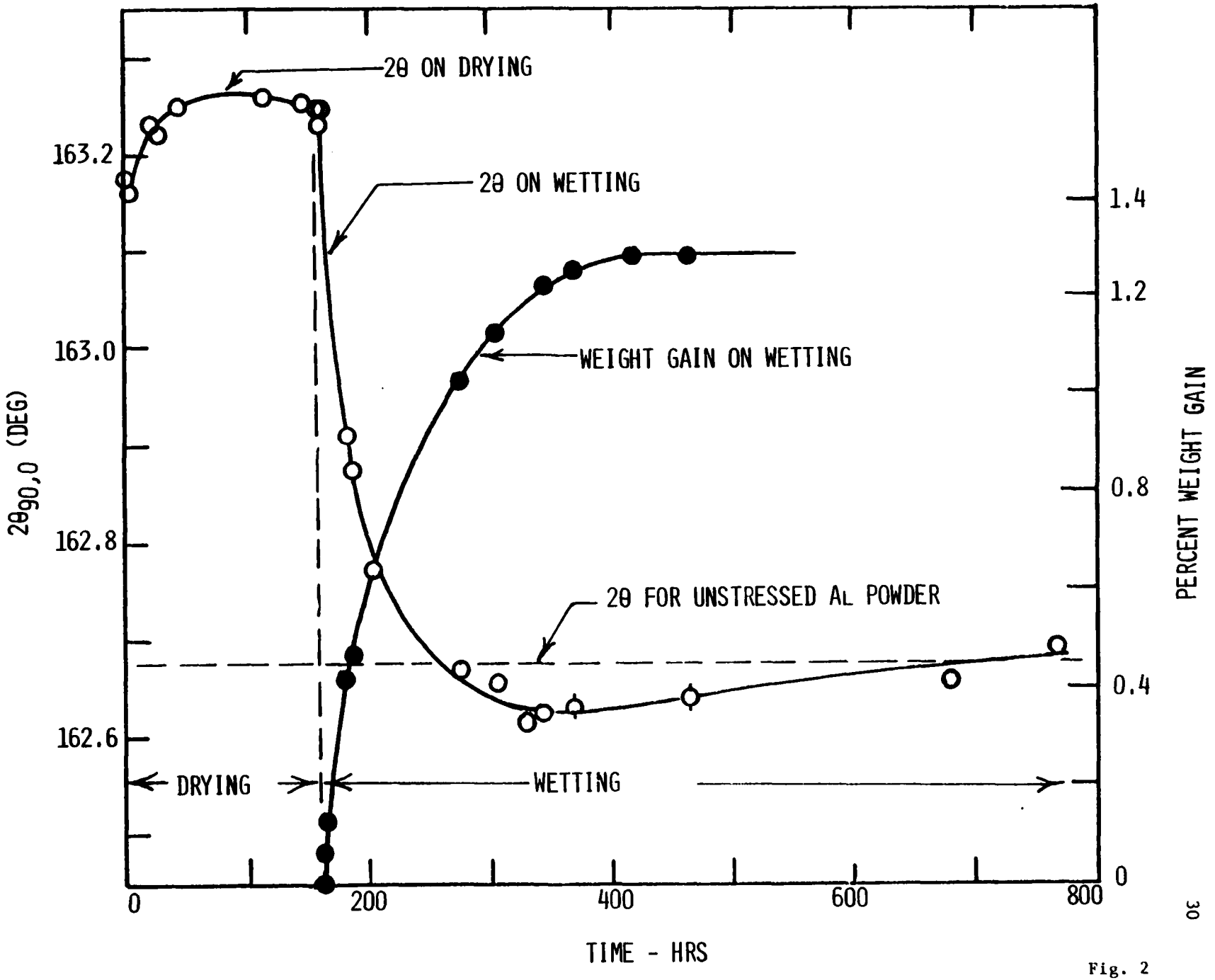
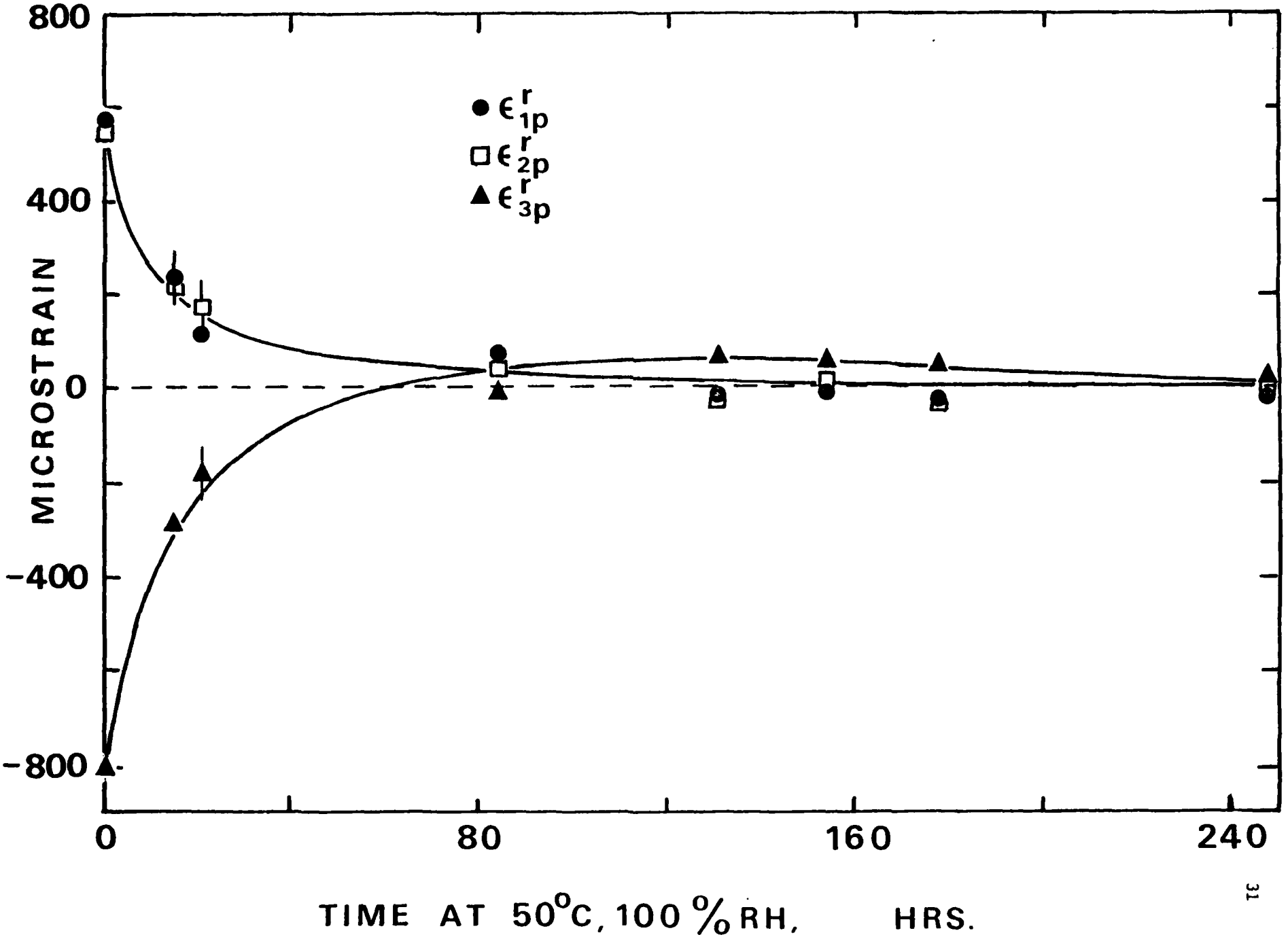

2θ ON DRYING
2θ ON WETTING
WEIGHT GAIN ON WETTING
2θ FOR UNSTRESSED AL POWDER
DRYING
WETTING
163.2
163.0
162.8
162.6
$2\theta_{90,0}$ (DEG)
1.4
1.2
0.8
0.4
0
PERCENT WEIGHT GAIN
0
200
400
600
800
TIME - HRS

Fig. 2


800
400
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-400
-800
MICROSTRAIN
ϵ^r_{1p}
ϵ^r_{2p}
ϵ^r_{3p}
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160
240
TIME AT 50°C, 100 % RH, HRS.

Fig. 3

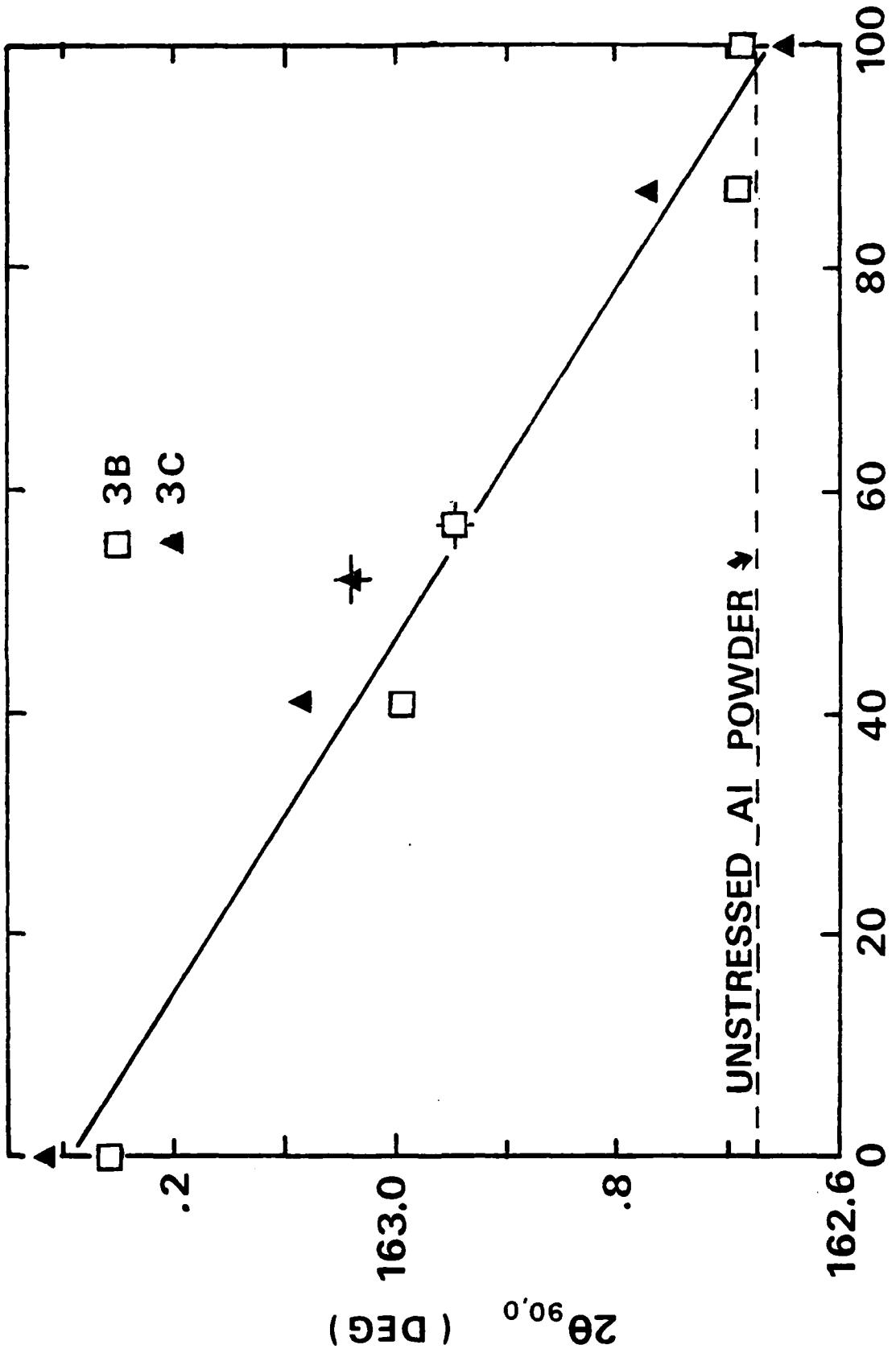

3B
3C
UNSTRESSED AI POWDER
% R.H.
0
20
40
60
80
100
162.6
163.0
.2
.8
$2\theta_{90.0}$ (DEG)

Fig. 4

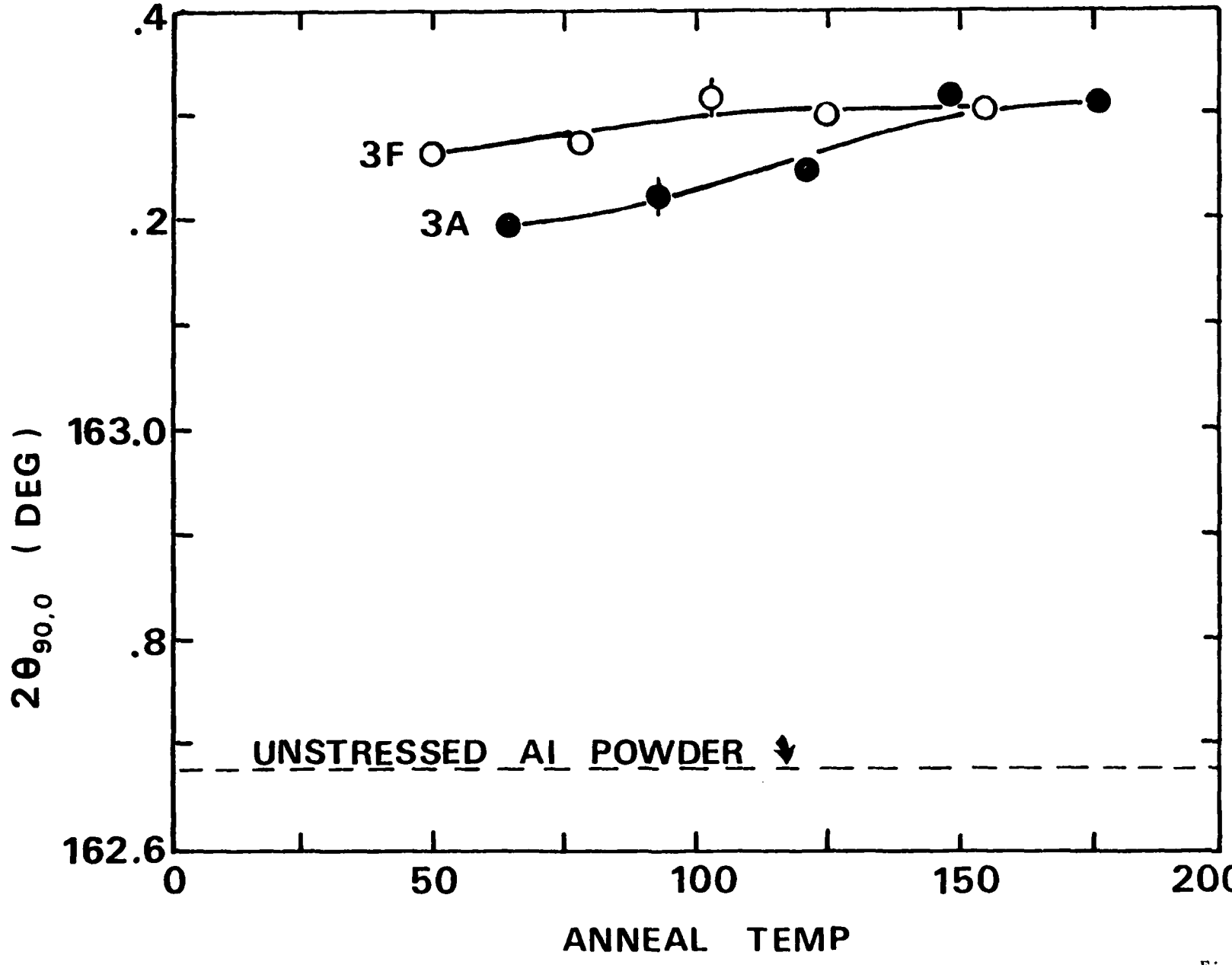
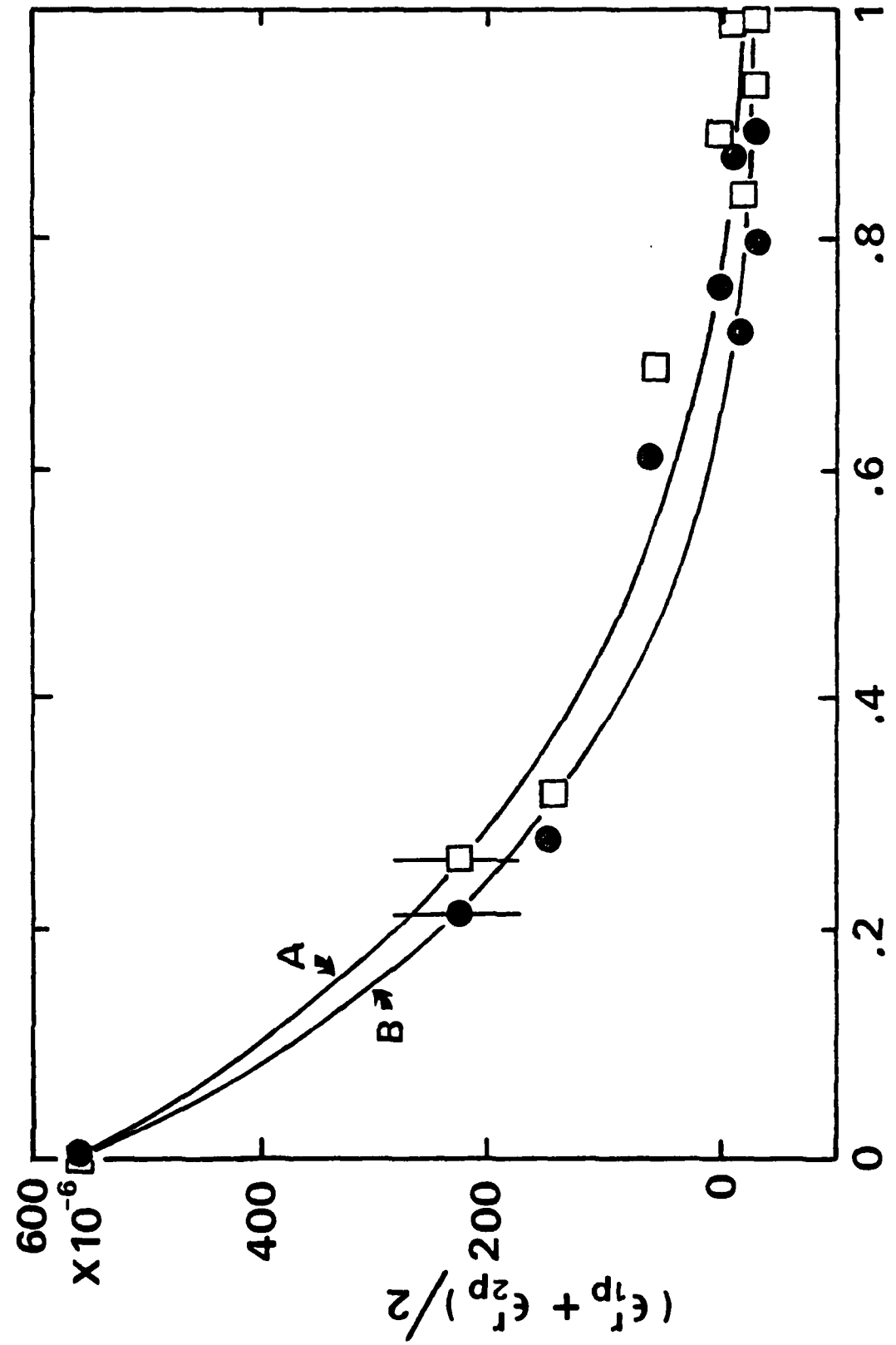

.4
.2
163.0
.8
162.6
$2\theta_{90,0}$ (DEG)
3F
3A
UNSTRESSED AI POWDER
0
50
100
150
200°C
ANNEAL TEMP

Fig. 5


600
400
200
0
$\times 10^{-6}$
$(\epsilon''_{1p} + \epsilon''_{2p})/2$
A
B
0
.2
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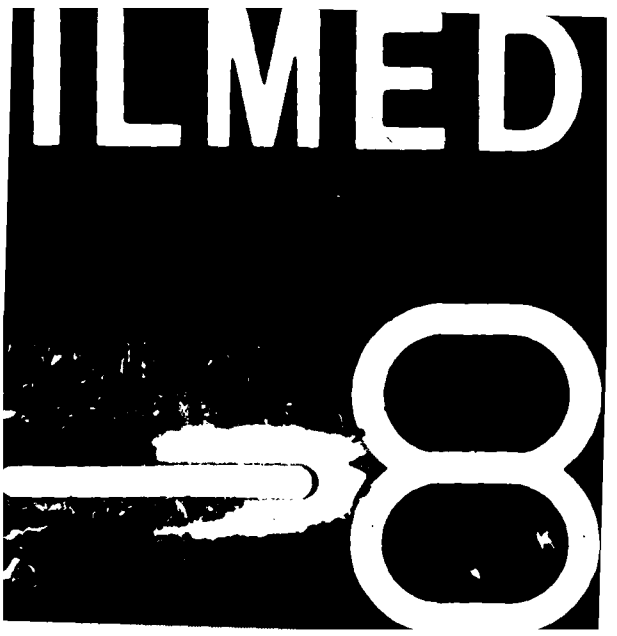
.6
.8
1
$\bar{C}/C_f$ or $C(x_p,t)/C_f$

Fig. 6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